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(56) Documents cited
GB 2226050 A GB 2206358 A GB 2159838 A
EP 0266299 A2 EP 0185603 A1 US 4851300 A

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(54) **Metal/ceramic protective coating for superalloy articles**

(57) A metal/ceramic protective coating as illustrated in Fig 1 for superalloy articles comprises an outer ceramic layer (1) comprising metal oxides; an oxidation-resistant layer (2) comprising an M–Cr–Al–Y alloy, where M comprises Ni, Co, Fe, or a combination thereof, with an Al content in the oxidation-resistant layer (2) of 7.5–14.0% by weight; and an inner plastic layer (3) comprising an M–Cr–Al–Y alloy, where M comprises Ni, Co, Fe, or a combination thereof, with an Al content in the inner plastic layer of 2.5–5.5% by weight, lying between the oxidation-resistant layer (2) and the surface of a superalloy article (4), wherein the ratio of thicknesses of the oxidation-resistant layer (2) and the inner plastic layer (3) is 4.0–1.0. The ceramic layer may be formed of yttria-stabilized zirconia which may contain TiB_2, ZrB_2, HfB_2, or Ce_2S_3. In addition there may be an aluminide layer between the inner plastic layer and the surface of the superalloy article. The coated product finds use as gas turbine blades or in parts for internal combustion engines.

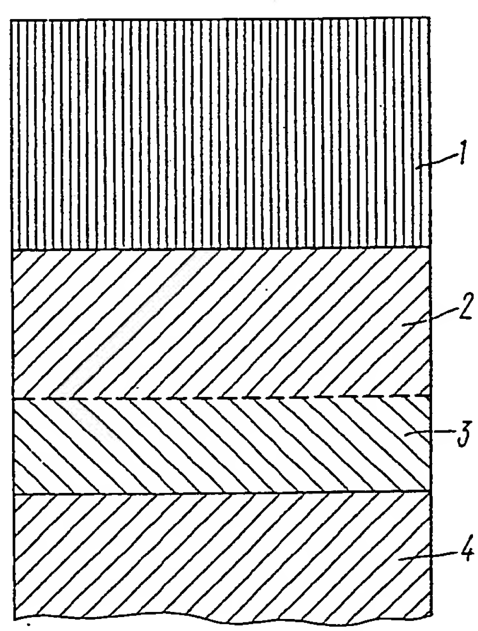

FIG.1

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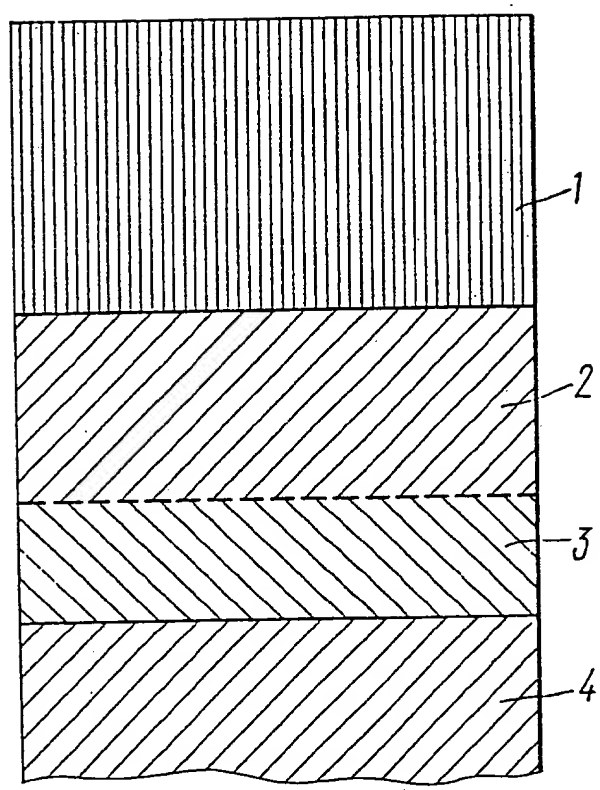

FIG.1

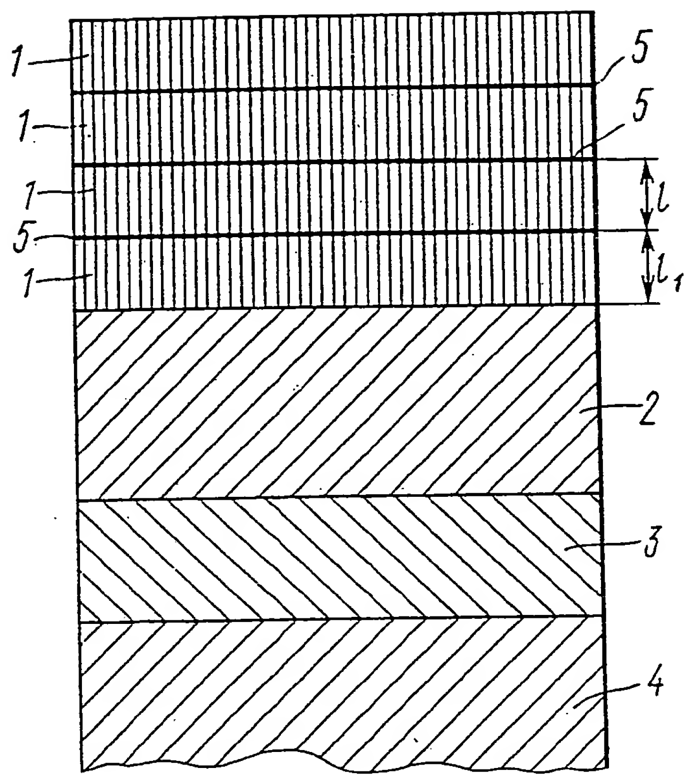

FIG. 2

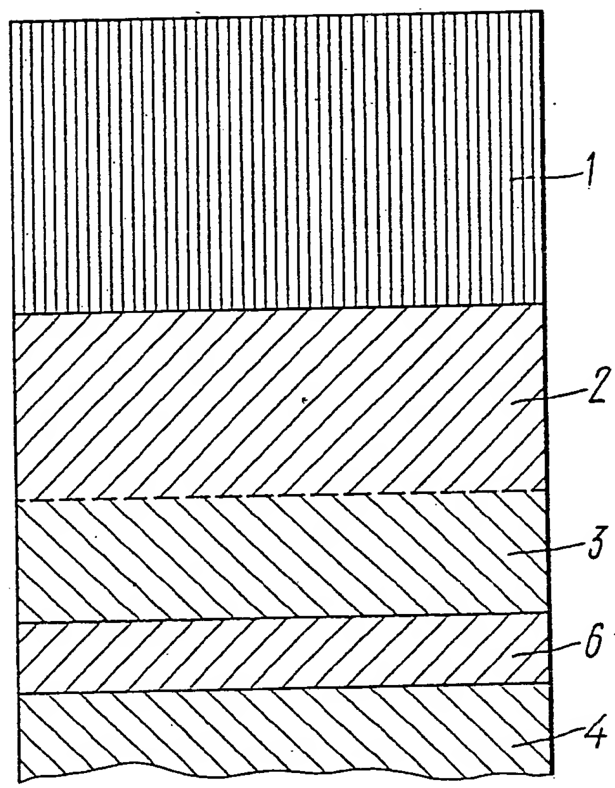

FIG.3

METAL/CERAMIC PROTECTIVE COATING FOR SUPERALLOY ARTICLES

The present invention relates to high-temperature coatings for metallic materials, and more particularly - to a protective coating of the metal/ceramic type for articles from superalloys, for example, gas turbine blades and parts of internal combustion engines.

The claimed invention finds application as a protective coating on blades and vanes of aircraft and marine gas turbines, hot parts of industrial gas turbines, for piston crowns of high-power diesel engines, and parts used in units for the production of synthetic fuels.

Parts of modern high-temperature equipment made from superalloys, e.g. blades of gas turbines, in the process of operation, are subjected to high-temperature and low-temperature corrosion, as well as to the action of cyclically changing thermal and mechanical loads. Compounds of sulfur, sodium salts, chlorides, lead, vanadium impurities, solid particles (carbon) contained in a gas flow cause growing corrosion and erosion failures of the working surface of non-protected parts.

Known in the art is a monolayer metal coating composed of M-Cr-Al-Y (where M is nickel, cobalt, iron taken separately or in combination).

A tendency to an increase of power, economy and ecological purity of modern engines and units has led to an increase of temperature of a gas flow (over 1,300°C)

and, accordingly, to a rise of working temperature of cooled parts. In connection with this, employment of the existing types of monolayer metal coatings becomes low efficient because of their fast failure, corrosion and erosion.

The effect of an aggressive high-temperature gas flow on a superalloy can be limited by developing thermal barrier coatings of the metal/ceramic type. Structurally, such coatings represent a two-layer system in which an oxidation-resistant layer composed of M-Cr-Al-Y is applied onto a protected part made from a superalloy; an outer ceramic layer made from a low heat-conducting oxide (as a rule, on the basis of stabilized zirconia) is applied onto the first layer.

A low heat conduction of the outer ceramic layer (by an order lower than that of the metal oxidation-resistant layer and of the superalloy - the part's material) in the employment of thermal barrier coatings makes it possible to lower the temperature of the part's metal, thus enhancing its life time or, maintaining the temperature of the metal's surface at the same level, to increase the temperature of gas, thereby increasing the engine power.

The basic functions of the oxidation-resistant layer in the two-layer thermal barrier coating of the metal/ceramic type reside in protection against oxidation and corrosion and providing an adhesive contact

with ceramics, while those of the outer ceramic layer reside in limiting the heat flow coming from the combustion products to the material of a part, preventing access of the aggressive gas-slag medium to the surface of the oxidation-resistant layer and in protecting it against erosion damage.

The main difficulty on the way of broad employment of coatings of the metal/ceramic type is an insufficiently high thermal cyclic life time (thermal shock resistance) of such coatings, ile. ability of the outer ceramic layer to endure cyclic temperature changes without delamination.

Residual stresses occurring due to mismatch between coefficients of thermal expansion of the outer ceramic layer (α_{ZrO_2} $10 \cdot 10^{-6} {}^{\circ}C^{-1}$) and oxidation-resistant layer ($\alpha_{M-Cr-Al-Y}$ $13-15 \cdot 10^{-6} {}^{\circ}C^{-1}$) can lead to spalling of ceramics. Known in the art is a protective coating and a method of its obtaining (plasma spraying) in which, in order to decrease residual stresses occurring due to mismatch between coefficients of thermal expansion of ceramics and metal, transition from the oxidation-resistant layer to the outer ceramic one occurs stepwise, i.e. the content of the oxide phase varies from 0 (at the surface of the oxidation-resistance layer M-Cr-Al-Y) to 100% (at the surface of the outer ceramic layer). In the course of operation of the abovementioned coating, oxidation of metal particles present in a ceramic matrix

is accompanied by expansion of their volume and finally results in a failure of the ceramic layer.

To prevent polymorphic transformations in the ceramic layer of zirconia (accompanied by considerable volumetric changes and cracking), use of yttria as a stabilizing oxide is most preferable owing to its high thermal stability, as compared with other oxides.

As a rule, the content of yttria in zirconia equals 6 - 20% by mass. The data available testify to the fact that the highest thermal shock resistance of ceramic coatings is attained at introducing 6-8% by mass of yttria in zirconia.

The key role in ensuring a high thermal cyclic life time of the outer ceramic layer is played by its microstructure, which is determined by a method of deposition of coatings.

For plasma-sprayed coatings characteristic is a lamellar microstructure of the outer ceramic layer. Coatings obtained by evaporation and condensation in vacuum have a microstructure in the form of columnar grains orientated along the normal to the surface on which they are deposited. It has been established that in its ability for resistance without failure of deformation and for relaxation of arising stresses, as well as in thermal shock resistance, the vapor-deposited ceramic coatings surpass those obtained by plasma-spraying.

Known in the art is a thermal barrier coating

which is a two-layer system obtained by electron-beam evaporation and vapour-deposition in vacuum. An outer ceramic layer from yttria-stabilized zirconia, 125 μm thick, applied over the oxidation-resistant layer (Ni - 23% by mass Co - 18% by mass Cr - 12.5% by mass Al - 0.3% by mass Y), owing to its microstructure, surpasses in thermal shock resistance a similar plasma-sprayed coating more than 20 times. Deposition of the outer ceramic layer is done on an alumina layer (Al_2O_3), 0.25-2.5 μm thick, preliminarily formed by oxidizing the oxidation-resistant layer (Ni-Co-Cr-Al-Y), which increases adhesion bond between the oxidation-resistant layer and the outer ceramic layer owing to processes of solid solubility.

Along with a high deformation ability, the vapour-deposited ceramic coatings have a disadvantage, connected with the fact that the surrounding medium can penetrate through intercolumnar gaps to the surface of the oxidation-resistant layer, rendering it oxidized and corroded.

It has been established that the main reason for delamination and spalling of the outer ceramic layer is oxidation of the surface of the oxidation-resistant layer, formation and growing of a layer of alumina Al_2O_3 on the metal/ceramic interface. At reaching a definite critical thickness, the layer of alumina Al_2O_3 starts delamination at thermal cycles, under the action of high compressive stresses, from the surface of the oxida-

tion-resistant layer M-Cr-Al-Y and spalling together with the outer ceramic layer.

It is an object of the present invention to create such a protective coating of the metal/ceramic type for articles made from superalloys which possesses an enhanced thermal cyclic and corrosion life time.

The above object is accomplished due to the fact that claimed is a protective coating of the metal/ceramic type for articles made from superalloys, which is a multilayer system containing an outer ceramic layer on the basis of metal oxides and an oxidation-resistant layer from the alloy M-Cr-Al-Y, where M is Ni, Co, Fe, taken separately or in combination, with the content of aluminium in the oxidation-resistant layer of 7.5-14.0% by mass, which, according to the invention, also contains an inner plastic layer from the alloy M-Cr-Al-Y, where M is Ni, Co, Fe, taken separately or in combination, with a content of 2.5-5.5% by mass of aluminium in the inner plastic layer located between the abovementioned system, comprising the outer ceramic layer and the oxidation-resistant layer, and the surface of an article made from a superalloy, the relation of thicknesses of the oxidation-resistant layer and the inner plastic layer being 4.0-1.0.

The claimed coating ensures extension of the service life of articles made from superalloys, e.g. blades of gas turbines by 1.5-2.0 times as compared with the

earlier used known two-layer coatings of the metal/ceramic type due to increased thermal stability and relaxation ability of the three-layer coating, retardation of the rate of growing of the layer of alumina Al_2O_3 on the metal/ceramic interface.

In case when the outer ceramic layer on the zirconia basis contains yttria as a stabilizer, it is recommended that the layer should also contain one of diborides of metals of the subgroup IYa of the Mendeleev's periodic system of elements (titanium diboride, or zirconium diboride, or hafnium diboride), with the following relation of components, % by mass:

TiB_2, or ZrB_2, or HfB_2 - 0.3 - 6.0;
Y_2O_3 - 5.0 - 25.0;
ZrO_2 - the balance.

Employment of three-layer coatings having a modified outer ceramic layer with additions of diboride of a metal of the subgroup IYa of the Periodic system of elements renders it possible to increase thermal shock resistance of coatings 2-3 times, as compared with non-modified outer ceramic layer of the three-layer coatings, and 3-4 times, as compared with the known tow-layer coatings of the metal/ceramic type.

In case of employment of yttria-stabilized zirconia as an outer ceramic layer, it is also recommended that it should additionally contain cerium sulfide, with the following relation of components, % by mass: Ce_2S_3 0.5-5.0;

Y_2O_3 6.0-25.0; ZrO_2 - the balance.

Employment of three-layer coatings with a modified outer ceramic layer, containing cerium sulfide, increases thermal cyclic life time of coatings 1.5-2.5 times, as compared with the known two-layer coatings.

It is also desirable that the outer ceramic layer on the yttria-stabilized zirconia basis should contain metallic zirconium in the form of interlayers 0.5-4.0 μm thick, located in the outer ceramic layer parallel to the article surface, the minimum distance between each of the interlayers, as well as the distance between the surface of the oxidation-resistant layer and the nearest to it interlayer of metallic zirconium being equal to 6.0 μm, and the number of interlayers of metallic zirconium being equal to at least one.

It is expedient that the outer ceramic layer of the yttria-stabilized zirconia basis should contain at least four interlayers of metallic zirconium, the thickness of each of which being equal to 2.5-3.0 μm, and the distance between each of the interlayers, as well as the distance between the surface of the oxidation-resistant layer and the nearest to it interlayer being equal to 20-23 μm.

The thermal cyclic life time of the three-layer coatings with an outer ceramic layer, containing interlayers of metallic zirconium, is 2.5-3.5 times higher than that of the known two-layer coatings of the metal/ceramic type.

Besides, it is also possible that the coating should contain a 5-45μm thick aluminide layer with 15-35% by weight aluminium located between the inner plastic layer and the surface of an article made from a superalloy.

Employment of such four-layer coatings for the protection of blades of gas turbines, operating under conditions of sulphide-oxide corrosion, enhances their thermal cyclic and corrosion life time 3-5 times, as compared with the earlier employed known two-layer coatings of the metal/ceramic type.

The invention will be further explained by a detailed description by way of example only, with reference to the accompanying drawings, wherein:

Figure 1 shows an article made from a superalloy with a protective coating applied thereon;

Figure 2 shows an outer ceramic layer of the protective coating shown in Figure 1;

Figure 3 shows a variant of the protective coating;

The protective coating of Figure 1 for articles made from superalloys is a multilayer system, containing an outer ceramic layer 1 on the basis of metal oxides, eg. ZrO_2, Al_2O_3, TiO_2 and Y_2O_3, an oxidation-resistant layer 2 from the alloy M-Cr-Al-Y, where M

is Ni, Co, Fe, taken separately or in combination, with the content of aluminium in this layer of 7.5-14.0% by mass, and an inner plastic layer 3 from the alloy M-Cr-Al-Y, where M is Ni, Co, Fe, taken separately or in combination, with the content of aluminium in this layer of 2.5-5.5% by mass. The inner plastic layer 3 is located between the oxidation-resistant layer 2 and the surface of an article 4 made from a superalloy. The relation of thicknesses of the oxidation-resistant layer 2 and the inner plastic layer 3 is 4.0 - 1.0.

The coating is produced by way of an electron beam-physical vapour deposition of various alloys M-Cr-Al-Y and ceramic materials with their vapour-deposition in vacuum on protected articles.

Deposition of coatings is performed by means of industrial electron-beam units, equipped with multi-crucible evaporators. The articles to be coated are placed in special fixtures intended for rotating the articles in a vapour flow of the evaporated material with a speed of 4-12 rpm. The articles are heated in a vacuum chamber by an electron beam to a temperature of 830 - 980°C. The temperature of the articles in the process of deposition of layers of M-Cr-Al-Y depends on the chemical composition of the superalloy from which an article is made. The pressure of residual gases in the vacuum chamber is maintained not over $1.3.10^{-2}$ Pa.

An ingot of the alloy M-Cr-Al-Y is placed in a

water-cooled crucible of the evaporator. The electron beam melts the ingot, forming a molten metal pool, and the vapour flow of the evaporated alloy starts condensation on the article surface, thus forming a protective coating.

The alloys Ni-Cr-Al-Y and Ni-Co-Cr-Al-Y are widely used for application of an oxidation-resistant layer owing to their phase stability. They are used, mainly, for the protection of blades of aircraft gas turbines, operating at a temperature of the gas exceeding 1,300°C, under conditions of frequent thermal cycles.

The systems of alloys Co-Cr-Al-Y and Fe-Cr-Al-Y are used for application of coatings operating under conditions of mainly sulfide-oxide corrosion, e.g. on blades of gas turbines of marine power units and on blades of gas-pumping units.

Application of a coating is started from deposition on the article's surface an inner plastic layer, containing 2.5-5.5% by mass aluminium from the alloy M-Cr-Al-Y.

The chemical composition of the inner plastic layer is selected, as a rule, close to that of the oxidation-resistant layer and differs from the latter only in a low content of aluminium, approximately corresponding ($\pm$0.5% by mass) to the content of aluminium in the superalloy, from which the article is made. The initial microstructure of the inner plastic layer must be close

to a single-phase one, i.e. practically, it should have no β-phase of MAl.

The thickness of the inner plastic layer is determined by the time of evaporation of the alloy.

Employment of a multicrucible evaporator makes it possible to apply an oxidation-resistant layer of the alloy M-Cr-Al-Y immediately after obtaining the inner plastic layer of the necessary thickness without extraction of articles from the vacuum chamber. The fixtures with articles are moved and placed over another crucible, wherein an ingot of the superalloy M-Cr-Al-Y was placed preliminarily. After that started is the process of deposition of the oxidation-resistant layer of the necessary thickness. The technological parameters of the process of application of the oxidation-resistant layer are identical to those employed in deposition of the inner plastic layer.

The rate of condensation of the inner plastic layer and oxidation-resistant layer on a rotating article depends on the chemical composition of the alloys M-Cr-Al-Y and equals 5-8 μm/min.

Upon application of the inner plastic layer and oxidation-resistant layer, the articles are removed from the vacuum chamber. Further on, they are subjected to a diffusion heat-treatment in vacuum at a temperature of 1,040-1,130°C for two hours, shot peening with metallic microballs, and then - to a repeated diffusion

heat treatment in vacuum for two-four hours at a temperature of 1,040-1,130°C (depending on the chemical composition of the superalloy from which the article is made).

The last stage is the formation, on the surface of the oxidation-resistant layer, an outer ceramic layer from yttria-stabilized zirconia. The main technological operations of articles' preparation are similar to those described above.

The fixtures with articles rotated at a speed of 4-12 rpm are arranged over the crucible of the evaporator, wherein located are the discs of compacted ceramics of stabilized zirconia. The temperature of articles in the course of deposition of the outer ceramic layer is maintained at the level of 850-1,080°C (which is determined by the chemical composition of evaporated ceramics and by the chemical composition of the superalloy from which an article is made).

Evaporation of ceramics is conducted at a rate of 0.9-3.5 μm/min. The outer ceramic layer consists of columnar grains and has a general porosity of 16-20%. The time of evaporation of the outer ceramic layer determines its necessary thickness on an article depending on functional tasks.

It has been established that introduction of the inner plastic layer M-Cr-Al-Y, containing 2.5-5.5% by mass aluminium, between the oxidation-resistant layer

M-Cr-Al-Y, containing 7.5-14.0% by mass aluminium, and the superalloy from which an article is made, considerably (2-4 times) increases thermal cyclic life time of the coating owing to retardation of the rate of growth of a layer of scale Al_2O_3, which is formed on the surface of the oxidation-resistant layer on the metal/ceramic interface, and relaxation of thermal stresses occurring in the three-layer system.

The obtained effect of increasing the thermal cyclic life time of the three-layer coating, as compared with the known two-layer coating, is explained by the following mechanism:

- presence of the inner plastic layer retards the interdiffusion action of the oxidation-resistant layer with the superalloy, the thickness of the diffusion zone, formed between them, being lowered. This considerably enhances thermal stability of the oxidation-resistant layer. A lower diffusion mobility of elements of the oxidation-resistant layer facilitates retardation of the rate of growth of a layer of alumina Al_2O_3;

- owing to its high plasticity because of a low content of aluminium, the inner plastic layer ensures relaxation of thermal stresses occurring at the metal/ceramic interface. In the long run, this increases the thermal cyclic life time of the coating.

The necessity of ensuring the maximum possible oxidation resistance and corrosion resistance of the

oxidation-resistant layer requires the presence of chromium (up to 24-26% by mass) and aluminium (up to 12-14% by mass in it) . However, at such amounts of these metals, resistance of thermal fatique the alloys M-Cr-Al-Y is lowered, especially so when the content of aluminium exceeds 14% by mass as a result of a temperature rise of the dictile-brittle temperature transition. Introduction of the inner plastic layer makes it possible to improve thermoplastic characteristics of the three-layer system. Owing to the ability of the inner plastic layer to retard thermal fatigue microcracks originating in the oxidation-resistant layer, the resistance of articles provided with such coatings to thermal fatigue is increased.

The necessary level of resistance to oxidation and corrosion is ensured at the introduction of 7.5-14% by mass aluminium into the oxidation-resistant layer. When the content of aluminium in the oxidation-resistant layer is less then 7.5% by mass, its resistance to oxidation at the operating temperature of over 1,000°C sharply drops.

The minimum content of aluminium in the inner plastic layer is 2.5% by mass, which is brought about by the fact that at lower amounts of it the exchange diffusion processes between the inner plastic layer and oxidation-resistant layer start to proceed intensitvely. The inner plastic layer loses the function of a diffusion

barrier, which lowers the effect of its employment.

With a content of aluminium in the inner plastic layer in excess of 5.5% by mass, due to a drop of plasticity, it loses relaxation properties, as a result of which its positive effect on the thermal cyclic life time vanishes.

The content of aluminium in the amount of 2.5-5.5% by mass in the inner plastic layer ensures a better thermal stability of the oxidation-resistant layer, as compared with the known two-layer coating of the metal/ceramic type. The growth of a layer of alumina Al_2O_3 is retarded and relaxation of thermal stresses occurring in the coating is facilitated, owing to which fact the thermal cyclic life time of the three-layer system is extended.

The outer ceramic layer of the three-layer coating, having a columnar microstructure with intercrystalline pores, is permeable for the surrounding oxidation medium. Owing to a decreased gas permeability of the outer ceramic layer, there appears a possibility to retard the rate of growth of the layer alumina Al_2O_3 and to increase the thermal stability of the protective coating.

Various oxides, such as e.g. CaO, MgO, CeO_2 and Y_2O_3 can be used as stabilizers of zirconia. In case of its stabilization by yttria, in order to decrease gas permeability of the outer ceramic layer, introduced into it is one of diborides of the metals of subgroup IVa

of the Periodic system of elements, with the following relation of the abovementioned components, % by mass: TiB_2 or ZrB_2 or HfB_2 0.3-6.0; Y_2O_3 5.0-25.0; ZrO_2 the balance.

Application of the coating is performed similarly to that described above, the only difference being that the evaporated ceramic discs contain a preliminarily introduced diboride of the metal of subgroup IVa of the Periodic system of elements.

The technology of producing ceramic discs is the following: the initial powders ZrO_2, Y_2O_3 and (TiB_2 or ZrB_2 or HfB_2), taken in the necessary per cent proportion, are mixed and compacted.

The temperature of an article in the process of application of the outer ceramic layer is at the level of 850-1,080°C and is determined by the chemical composition of ceramics and superalloy, from which the article is made.

The deposited outer ceramic layer ZrO_2 - Y_2O_3 - (TiB_2 or ZrB_2 or HfB_2) has disperse particles of the introduced diboride uniformly distributed throughout the entire volume of ceramics, said particles being mainly released along the borders of columnar crystallines.

In the course of operation of the coated articles, at heating the outer ceramic layer over 900°C, there occurs oxidation of diboride particles with the forma-

tion of molten boric anhydride B_2O_3 in the form of accumulations of a vitreous film along the borders of columnar crystallines, microcracks and pores. This film creates a diffusion barrier for penetration of the aggressive medium along the borders of columnar crystallines through the outer ceramic layer. Its gas permeability is decreased, the growth of a layer of alumina Al_2O_3 on the metal/ceramic interface is retarded, as a result of which the general thermocyclic life time is increased.

Besides, owing to a modifying effect of diborides, the microstructure of the outer ceramic layer becomes more disperse. The number of columnar crystallines is increased, while the size of the cross section of a single crystalline is decreased. This impedes the spread of microcracks in the outer ceramic layer, appearing under the action of thermal stresses.

The percentage of ingredients of the outer ceramic layer is determined by the operating conditions of articles and chemical composition of the oxidation-resistance layer.

With a content of diboride of one of the metals of subgroup IVa of the Periodic system of elements less than 0.3 and more than 6.0% by mass, the positive effect of increasing thermal stability practically boiled down to a minimum. This is associated with the fact that with a content of titanium diboride (or zirconium diboride or hafnium diboride) in excess of 6.0% by mass, there

occurs an increase of the volume fraction of diboride particles released in the ceramic matrix, their size is increased, bringing about the appearance of microgaps in the outer ceramic layer. With a content of one diboride of the metals of subgroup IVa of the Periodic system of elements less then 0.3% by mass, the amount of released disperse particles is too small for creating diffusion barriers on the way of the oxidation medium in the outer ceramic layer.

Lowering of gas permeability in the outer ceramic layer from yttria-stabilized zirconia can also be attained at introducing cerium sulfide in it, with the following percentage of components, % by mass: Ce_2S_3 0.4–5.0; Y_2O_3 6.0 - 25.0; ZrO_2 - the balance.

Application of the coating is performed similarly to that described above, the only difference being that the evaporated ceramic discs contain cerium sulfide introduced preliminarily.

Taken in the necessary percentage, the initial powders of zirconia, yttria and cerium sulfide are mixed and compacted into ceramic discs.

The temperature of an article in the process of application of the outer ceramic layer is at the level of 850 - 1,080°C and is determined by the chemical composition of ceramics and superalloy from which the article is made.

The positive effect of cerium sulfide resides in ensuring the formation of dense intercrystalline inter-

faces of the outer ceramic layer. Acting as a plasticizing phase that reduces microhardness of the outer ceramic layer, cerium sulfide noticeably makes the structure finer and increases uniformity of axes of columnar crystallines, due to which fact they grow together more closely. There are no discontinuities along intercrystalline interfaces. As a result, gas permeability of the outer ceramic layer becomes less, the growth of a layer of alumina Al_2O_3 is retarded, and thermal shock resistance of the outer ceramic layer is increased.

With the content of cerium sulfide in the outer ceramic layer less than 0.5% by mass, a sufficiently dense intergrowth of columnar crystallines is not ensured, whereas with the amount of it in excess of 5.0% by mass, the structure of the outer ceramic layer becomes excessively dense. Microcracks appear in the outer ceramic layer which decrease resistance to oxidation and thermal shock resistance of the coating.

Further increase of thermocyclic life time of the outer ceramic layer owing to lowering of gas permeability is asociated with a change (violation) of its columnar structure.

This is accomplished by that the outer ceramic layer I (Fig. 2) applied on the oxidation-resistant layer 2, also contains at least one interlayer 5 of metallic zirconium with a thickness of 0.5-4.0 μm arranged

parallel to the article, the distance l between each of interlayers 5 of metallic zirconium and the distance l_1 between the surface of the oxidation-resistance layer 2 and the interlayer 5 of metallic zirconium, nearest to the layer 2, must equal 6 μm, or more.

Introduction of interlayers 5 from metallic zirconium makes it possible to increase thermal cyclic life time of three-layer coatings. Especially efficient is introduction of such interlayers into the outer ceramic layer from yttria-stabilized zirconia with a modifying addition of one of diborides of metals of subgroup IVa of the Periodic system of elements, or cerium sulfide.

Application of the coating is performed according to the technology described above, the only difference being that in the deposition of the outer ceramic layer I, periodically (depending on the required amount of interlayers 5 of metallic zirconium) stopped is evaporation of ceramics and displaced is the fixture with articles, which is arranged over the crucible that contains metallic zirconium. Zirconium is melted by means of an electron beam and an interlayer 5 of the required thickness is deposited. Then evaporation of metallic zirconium is stopped, the fixture with articles is displaced and located over the ceramics, and deposition of the outer ceramic layer I is resumed. After a definite period of time (required for application of the outer

ceramic layer with a thickness equal to the distance 1 between the neighbouring interlayers) the whole technological cycle of deposition of the next interlayer 5 of metallic zirconium is repeated.

Introduction of interlayers of metallic zirconium breaks the columnar structure of grains and decreases porosity of the outer ceramic layer. Owing to this, gas permeability of the outer ceramic layer is lowered, while the rate of formation and growth of a layer of alumina Al_2O_3 on the metal/ceramic interface is retarded.

In the course of operation of an article with the claimed coating, as a result of penetration of an oxidizing medium, there occurs a subsequent (beginning from the interlayer nearest to the surface of the outer ceramic layer) oxidation of interlayers of metallic zirconium and their transformation into interlayers of zirconia. The interlayers of zirconia, thus formed, serve as barriers on the way of penetration of an aggressive gas medium and retard the process of oxidation and corrosion of the oxidation-resistant layer. Thereby, accomplished are retardation of the rate of growth of a layer of alumina Al_2O_3 and extension of the thermal cyclic life time of the coating. An interval of thickness of each of the interlayers 5 of metallic zirconium of 0.5-4.0 μm is determined by the type and conditions of operation of an article made from a superalloy, as well as by the thickness of the outer ceramic layer. At a thickness

of the interlayer exceeding 4.0 μm, a probability arises of appearance of a local separation of ceramics from metallic zirconium in the process of operation. At a thickness of the interlayer of metallic zirconium less than 0.5 μm, the effect from their introduction into the outer ceramic layer sharply drops, since they are already not a sufficiently effective barrier on the way of the oxidation medium owing to its small thickness.

If the distance between interlayers of metallic zirconium and the distance between the surface of the oxidation-resistant layer and the interlayer nearest to it becomes less then 6 μm, a danger appears of delamination of the outer ceramic layer at thermal cycles because of the appearance of considerable thermal stresses in the outer ceramic layer.

The number of introduced interlayers 5 is determined by the geometry of the surface and operating conditions of an article subjected to coating, as well as by the thickness of a single interlayer and the thickness of the outer ceramic layer.

For the articles of a complex shape with inner cavities, with a view to enhance resistance to oxidation and thermalc cyclic life time, offered is a multilayer coating, containing in addition to the abovementioned outer ceramic layer I (Fig. 3), the oxidation-resistant layer 2 and the inner plastic layer 3, an aluminide layer 6, with the thickness of 5-45 μm, having 15-35% by mass aluminium and located between the superalloy from which

the article 4 is made, and the inner plastic layer 3. The aluminide layer 6 is produced by a diffusion saturation, as well as by means of other known technologies.

The technology of deposition of a three-layer coating on the surface of an article made from a superalloy, having an aluminide layer, does not differ from that described above.

A positive effect of the aluminide layer is brought about, first of all, by reducing thermal stresses in the oxidation-resistant layer on the metal/ceramic interface, which enhances the thermal cyclic life time of the coating. This is accomplished owing to the appearance in the aluminide layer, when cooled, residual compressive stresses, since its coefficient of thermal expansion is lower than that of the superalloy. When the oxidation-resistant and inner plastic layers are cooled, residual tensile stresses appear in these layers, since their thermal coefficient of linear expansion is greater than that of the superalloy. As a result of a mutual compensation, the general level of stresses in such four-layer system is lowered, which facilitates the increase of the thermal cyclic life time of the coating.

Resides, the aluminide layer acts an an additional diffusion barrier, materially limiting the diffusion interaction of the three-layer coating with the superalloy, which increases the thermal stability and life time of the coating.

The maximum content of aluminium in the aluminide layer (35% by mass) is determined by the fact that exceeding of this level leads to worsening of mechanical characteristics of the superalloy, in the first place, of the thermal fatigue ones.

The minimum value of content of aluminium in the aluminide layer (15% by mass) is associated with the fact that at a lower concentration the aluminide layer lowers its oxidation resistance at a temperature exceeding 950°C. At a thickness of the aluminide layer less than 5 μm, its action practically is not felt because of inability to redistribute residual stresses.

At a thickness over 45 μm the aluminide layer may start cracking because of considerable compressive stresses acting therein.

Employment of the coating to protect blades of a gas turbine of a marine power unit operating at a temperature over 920°C under conditions of a sulfide-oxide corrosion makes it possible to extend their service life almost twice, as compared with two-layer metal/ceramic coatings employed ealier.

Employment of three-layer coatings with an outer ceramic layer from yttria-stabilized zirconia, containing stabilizing additions (one of diborides of the metals of subgroup IVa of the Periodic system of elements or cerium sulfide) to protect blades of an aircraft gas turbine operating at a temperature of a gas flow of

1,300°C-plus makes it possible to increase their thermal cyclic life time three times in comparison with blades protected by the known two-layer metal/ceramic coating.

Application of three-layer coatings with an outer ceramic layer containing interlayers of metallic zirconium on piston crowns of an adiabatic diesel engine with an elevated temperature of fuel combustion products increases their thermal cyclic life time 3.5 times, as compared with piston crowns protected by the known two-layer metal/ceramic coating.

Employment of the coating, having an aluminide layer, on blades of gas turbines operating under conditions of a sulfide-oxide corrosion, extends their thermal cyclic and corrosion life time four times, as compared with the known two-layer coatings of the metal/ceramic type.

Given below are concrete examples, illustrating the invention.

EXAMPLE I. A three-layer coating of the metal/ceramic type, containing an inner plastic layer Ni - 17.2% by mass Cr - 5.5 % by mass Al - 0.1% by mass Y, 50 μm thick, an oxidation-resistant layer Ni - 17.4% by mass Cr - 14.0% by mass Al - 0.1% by mass Y, 50 μm thick, and an outer ceramic layer ZrO_2 - 8% by mass and Y_2O_3, 100 μm thick, is applied on a group of blades of an aircraft gas turbine (the length of the blade fin is 90 mm) made from an alloy, containing, % by mass:

Cr 8.0 - 9.5; W 9.5 - 11.0; Co 9.0 - 10.5; Al 5.1 - 6.0; Mo 1.2 - 2.4; Ti 2.0 - 2.9; Nb 0.8 - 1.2 ; Fe $\leqslant$ 1.0; C 0.13 - 0.22; Ni - the balance.

Application of the coating is performed by means of an industrial electron-beam unit on blades rotating in a vapour cloud of the evaporated material at a speed of 6 rpm. Deposition of the inner plastic and oxidation-resistant layers is performed by way of a successive electron-beam evaporation of ingots 68.5 mm in diameter made from the alloys Ni-Cr-Al-Y of the respective chemical composition. The temperature of heating the blades in the process of deposition of metallic layers of the coating is 830$\pm$25°C, the rate of condensation of the layers Ni-Cr-Al-Y being 5.8 μm/min. The vacuum in the working chamber should not exceed $I.3 \cdot 10^{-2}$ Pa.

Upon application of the inner plastic and oxidation-resistant layers, the blades are subjected to a diffusion heat treatment in vacuum at a temperature of 1,040°C during 2 hours, after which, in order to obtain a dense, non-porous structure of the oxidation-resistant layer, they are subjected to shot peening with steel microballs 200 μm in diameter. Next, the blades are subjected to a repeated diffusion heat treatment in vacuum at a temperature of 1,040°C during 2 hours.

Application of the outer ceramic layer on the blades having the layers Ni-Cr-Al-Y is performed by way of an electron-beam evaporation of ceramic discs 68.5 mm in

diameter. In the process of deposition of ceramics, the temperature of blades is maintained at the level of $950 \pm 25^{\circ}C$, the rate of deposition of the outer ceramic layer being 1.9 μm/min, and vacuum in the working chamber being not in excess of $1.3 \cdot 10^{-2}$ Pa. Upon application of the outer ceramic layer, the blades are subjected to a diffusion heat treatment in vacuum at a temperature of 1,050°C during 2 hours. The general porosity of the outer ceramic layer, as measured by a gravimetric method is 19%, and an average diameter of a single columnar grain is 4.3 μm.

Thermal cyclic tests of the coated blades are performed in the open by way of heating them to a temperature of 1,100°C during 3 minutes, keeping them at this temperature during 5 minutes, and cooling to a temperature of 100°C during 0.5 minute. Appearance of the first cracks and spalling of the outer ceramic layer is considered a failure of the coating.

For the purpose of comparison, subjected to testing are the blades with a two-layer coating of the metal/ceramic type, including an oxidation-resistant layer Ni - 17.3% by mass Cr - 14.0% by mass Al - 0.1% by mass Y, 100 μm thick, and an outer ceramic layer ZrO_2 - 8% by mass Y_2O_3, 100 μm thick. The technological parameters of application of coatings are similar to those employed in application of three-layer coatings.

The average thermal cyclic life time of the blades with a three-layer coating is over 70 thermal cycles

(without failure) and that of the blades with two-layer coatings is only 23 thermal cycles.

EXAMPLE 2. A three-layer coating of the metal/ceramic type, including an inner plastic layer Co - 24.0% by mass Cr - 4.3% by mass Al - 0.1% by mass Y, 25 μm thick, an oxidation-resistant layer Co - 28.0% by mass Cr - 10.2% by mass Al - 0.1% by mass Y, 100 μm thick, and an outer ceramic layer ZrO_2 - 12% by mass Y_2O_3, 180 μm thick, is applied onto cylindrical samples 7 mm in diameter (the length of the working part of the samples is 60 mm) made from a superalloy of the following composition, % by mass: Cr - 18.0; Co - 5.6 ; Al - 4.5; W - 4.0; Mo - 4.0; Ti - 2.6; Fe - 2.3; Ni - the balance.

Deposition of the coating is performed according to the technology described in Example 1. The general porosity of the outer ceramic layer is 21%.

Tests for thermal shock resistance are conducted in the open, observing the following conditions: heating of the coated samples to a temperature of 1,100°C during 4 minutes, keeping them at the maximum temperature during 20 minutes, and cooling by a flow of air to a temperature of 40°C during 6 minutes. Spalling of the outer ceramic layer on an area of 50% of the sample surface is considered a failure of the coating.

The thermal cyclic life time of the samples with a three-layer coating is 175 thermal cycles, whereas the samples made from the similar alloy with a two-layer

coating, including an oxidation-resistant layer Co - 28.0% by mass Cr - 10.1% by mass Al - 0.1% by mass Y, 125 μm thick, and an outer ceramic layer ZrO_2 - 12% by mass Y_2O_3, 180 μm thick, applied with the use of the same technological parameters, endure only 90 thermal cycles.

Tests of the samples with two-layer and three-layer coatings for oxidation resistance (oxidation in the open at a temperature of 1,000°C) during 500 hours show that the thickness of a layer of alumina Al_2O_3 formed at the metal/ceramic interface of the three-layer coatings is 2.0 μm, while in the two-layer coatings it is equal to 3.0 μm.

The thickness of a diffusion zone between the oxidation-resistant layer and the inner plastic layer of the three-layer coatings 20 μm, and of thet between the oxidation-resistant layer and the superalloy of the two-layer coating - 45 μm.

EXAMPLE 3. A three-layer coating of the metal/ceramic type, including an inner plastic layer Co - 24.8% by mass Cr - 4.0% by mass Al - 0.1% by mass Y, 40 μm thick, an oxidation-resistant layer Co - 26.9% by mass Cr - 11.7% by mass Al - 0.1% by mass Y, 50 μm thick, and an outer ceramic layer ZrO_2 - 12% by mass CeO_2, 110 μm thick, is applied onto wedge-shaped samples, simulating a leading edge of a blade (the leading edge corner radius of the samples being 0.7 mm, height - 80 mm, length - 43-47 mm) made from a superalloy of the

composition given in Example 2, on whose surface on aluminide layer (30% by mass Al), 30 μm thick, was applied earlier by the gas-phase deposition method.

The technology of deposition of the three-layer coating is similar to that described in Example 2.

The rate of condensation of metallic layers of the coating is 5.0 μm/min, and that of the outer ceramic layer - 2.2 μm/min. The general porosity of the outer ceramic layer is 23%.

The samples are subjected to thermal cyclic tests on a gas-dynamic stand in the diesel fuel combustion products, containing 0.25% by mass sulfur. The maximum temperature of the blade leading edge of the samples is 1,000°C. The time of heating up to this temperature is 60 s., the time of cooling down to a temperature of 400°C is 70 s. The amplitude of thermal stresses (a sum of tensile and compressive stresses), owing to different length of the samples, is equal to 815-955 MPa.

The formation of a thermal fatigue crack, 0.5 mm long, on a leading edge is considered a start of the coating failure, while the life time is determined by the number of thermal cycles up to the formation of such a crack.

The thermal cyclic life time of the three-layer coatings is 790 thermal cycles, whereas the wedge-shaped samples with an aluminide layer, 30 μm thick, carrying a two-layer vapour-deposited overcoating, including an oxidation-resistant layer 90 μm thick, similar in composition to the oxidation-resistant layer

of the three-layer coating mentioned above, and an outer ceramic layer ZrO_2 - 12% by mass CeO_2, 100 μm thick, could endure only 400 thermal cycles.

A metallographic analysis of the failed samples has shown that the thickness of a layer of alumina Al_2O_3 which forms on the metal/ceramic interface of the three-layer coatings, does not exceed 2.5 μm, which is almost 1.5 times less in comparison with the thickness of a layer of alumina Al_2O_3 that forms in two-layer coatings.

EXAMPLE 4. A three-layer coating of the metal/ceramic type, including an inner plastic layer Ni - 10.5% by mass Co - 17.4% by mass Cr - 4.8% by mass Al - 0.2% by mass Y, 40 μm thick, an oxidation-resistant layer Ni - 11.2% by mass Co - 18.7% by mass Cr - 8.0% by mass Al - 0.1% by mass Y, 60 μm thick, and an outer ceramic layer ZrO_2 - 6% by mass Y_2O_3, 95 μm thick, is applied on small-size (the length of the blade fin is 25 mm) blades of an aircraft gas turbine from a superalloy, including, % by mass: Cr 10.0 - 12.0; Al - 5.0-6.0; W 4.5 - 5.5 ; Co 4.0 - 5.0; Mo 3.5 - 4.8; Ti - 2.5-3.2; Fe 2.0; C - 0.1 - 0.2 and Ni- the balance.

The technology of application of the coating is similar to that described in Example 1, the only difference being that the temperature of the samples in the process of deposition of the outer ceramic layer is 920 ± 25°C.

The rate of condensation of metallic layers of the coating is 5.6 μm/min, and that of the ceramic layer - 1.5 μm/min.

The thermal cyclic tests of the blades are conducted under conditions similar to those described in Example 2.

The thermal shock resistance of the claimed three-layer coatings is 460 thermal cycles, which is 1.7 times higher in comparison with the thermal shock resistance of the known two-layer coatings, including an oxidation-resistant layer, 100 μm thick, and an outer ceramic layer, 95 μm thick, similar in composition and conditions of application to the same system of a three-layer coating.

The thickness of a layer of alumina Al_2O_3 in a three-layer coating of the tested samples is 2.0 μm, and that in a two-layer coating - 2.5 μm.

EXAMPLE 5. A three-layer coating, including an inner plastic layer Ni - 15.0% by mass Cr - 4.2% by mass Al - 0.1% by mass Y, 40 μm thick, an oxidation-resistant layer Ni - 17.8% by mass Cr - 10.7% by mass Al - 0.1% by mass Y, 50 μm thick, and an outer ceramic layer Al_2O_3 - 10% by mass ZrO_2, 80 μm thick, is applied on the samples made from a superalloy (the shape of the samples and composition of the superalloy are given in Example 2).

Deposition of the coating is performed according to

the technology described in Example 1. The temperature of the samples in the process of deposition of the outer ceramic layer is 990±25°C, the rate of condensation of the outer ceramic layer - 1.2 μm/min.

The methods of testing for thermal shock resistance are described in Example 2.

The thermal cyclic life time of the samples with a three-layer coating is 58 thermal cycles, whereas the samples made from the similar alloy with a two-layer coating, including an oxidation-resistant layer Ni - 17.7% by mass Cr - 10.6% by mass Al - 0.1% by mass Y, 90 μm thick, and an outer ceramic layer Al_2O_3 - 10% by mass ZrO_2, applied under the same technological parameters endure only 37 thermal cycles.

EXAMPLE 6. A coating of the metal/ceramic type, including an inner plastic layer Fe - 20.2% by mass Ni - 16.1% by mass Cr - 2.5% by mass Al - 0.1% by mass Y, 30 μm thick, an oxidation-resistant layer Fe - 27.3% by mass Cr - 7.5% by mass Al - 0.1% by mass Y, 60 μm thick, and an outer ceramic layer ZrO_2 - 20% by mass Y_2O_3, 125 μm thick, is applied on the cylindrical samples, described in Example 2, made from a superalloy of the following composition, % by mass: Ni - 33-37; Cr 14-16; W 2.8 - 3.5 ; Ti 2.4 - 3.2 ; Al 0.7 - 1.4; Mn $\leqslant$0.6; Si$\leqslant$0.6; S$\leqslant$0.02; P$\leqslant$0.035; B$\leqslant$0.02; C$\leqslant$0.08; Fe - the balance.

The technological parameters of application of the coating are similar to those described in Example 1. The general porosity of the outer ceramic layer is 22%. The thermal cyclic tests are performed under conditions described in Example 2.

The thermal shock resistance of the three-layer coating is 180 thermal cycles, which is 1.8 times higher than that of the two-layer coating of the metal/ceramic type, having an oxidation-resistant layer with a thickness of 90 µm and an outer ceramic layer with a thickness of 125 µm, whose compositions are similar to those of the three-layer system.

EXAMPLE 7. Applied on the samples made from a superalloy, whose composition and dimensions are similar to those described in Example 2, is a three-layer vapour-deposited coating of the metal/ceramic type, including an inner plastic layer Ni - 17.4% by mass Cr - 3.7% by mass Al - 0.1% by mass Y, 35 µm thick, an oxidation-resistant layer Ni - 17.9% by mass Cr - 10.3% by mass Al - 0.1% by mass Y, 60 µm thick, and an outer ceramic layer ZrO_2 - 8% by mass Y_2O_3 - 1.6 by mass TiB_2, 90 µm thick.

The technological parameters of deposition of the three-layer coating are similar to those described in Example 1. Application of the outer ceramic layer by way of an electron beam evaporation of the ceramic material, containing zirconia, yttria and titanium

diboride, preliminarily mixed and compacted into discs 68.5 mm in diameter, located in one of the crucibles of the evaporator of the electron-beam unit.

The rate of condensation of metallic layers of the coating is 5.9 μm/min, and that of the outer ceramic layer - 2.5 μm/min. The general porosity of the outer ceramic layer is 17%, the average diameter of a single columnar grain is 2.2 μm.

The tests for thermal shock resistance are performed under conditions described in Example 2.

The thermal shock resistance of the samples with a three-layer coating, whose ceramic layer contains titanium diboride, is 710 thermal cycles, while that of a three-layer coating without titanium diboride in the outer ceramic layer is 350 thermal cycles; the thermal shock resistance of a two-layer coating, including an oxidation-resistant layer Ni - 17.7% by mass Cr - 10.3% by mass Al - 0.1% by mass Y, 95 μm thick, and an outer ceramic layer ZrO_2 - 8% by mass Y_2O_3, 90 μm thick, is 220 thermal cycles.

The metallographic analysis of the samples tested for oxidation resistance under conditions described in Example 2 has shown that the thickness of a layer of alumina Al_2O_3, which is formed in the three-layer coating with an outer ceramic layer from ZrO_2 - Y_2O_3 - TiB_2 does not exceed 1.8 μm, which is 1.5 times less than that in the three-layer coating, whose outer ceramic layer does

not contain titanium diboride, and 1.8 times less than that in the two-layer coating.

EXA..PLE 8. Applied on cylindrical samples made from a superalloy, whose dimension and composition are given in Example 2 and whose surface has a previously deposited aluminide layer, 45 μm thick, containing 15% by mass aluminium, is a three-layer coating, including an inner plastic layer Co -23.3% by mass Cr - 3.1% by mass Al - 0.1% by mass Y, 40 μm thick, an oxidation-resistant layer Co - 27.1% by mass Cr - 11.4% by mass Al - 0.1% by mass Y, 50 μm thick, and an outer ceramic layer ZrO_2 - 5% by mass Y_2O_3 - 6% by mass ZrB_2, 55 μm thick.

The technological parameters of deposition are similar to those described in Example 1. The temperature of the samples in the process of deposition of the outer ceramic layer is 900 $\pm$ 25°C. The rate of condensation of metallic layers of the coating is 5.5 μm/min, and that of the outer ceramic layer - 2.1 μm/min. The general porosity of the outer ceramic layer is 19%, the average diameter of a single grain is 2.8 μm.

The tests for thermal shock resistance have been performed under conditions described in Example 2.

Simultaneously, subjected to testing were the samples with the abovementioned three-layer coating, applied onto samples which had no aluminide layer, the samples with a four-layer coating (including the aluminide layer), similar in composition and thickness to the coating

described in this Example, in whose composition of the outer ceramic layer there were no zirconium diboride, as well as the samples with a two-layer coating of the metal/ceramic type, containing an oxidation-resistant layer, 90 μm thick, whose composition is similar to that used in the three-layer coating, and an outer ceramic layer ZrO_2 - 5% by mass Y_2O_3, 55 μm thick.

The thermal shock resistance of the four-layer coating with an outer ceramic layer, containing zirconium diboride, is 480 thermal cycles. The same coating, but without an aluminide layer, withstands 422 thermal cycles. The life time of the four-layer coating, whose outer ceramic layer contained no zirconium diboride, is 390 thermal cycles. The least thermal shock resistance (305 thermal cycles) has a two-layer coating of the metal/ceramic type.

EXAMPLE 9. Applied on the wedge-shaped samples made from a superalloy is a four-layer coating of the metal/ceramic type (the form of the samples, composition of the superalloy, composition and thickness of the coating are given in Example 3).

The coating differs only in that the thickness of the aluminide layer is 5 μm (the amount of aluminium is 35% by mass), and in that the outer ceramic layer has a composition ZrO_2 - 8% by mass Y_2O_3 - 1.9% by mass Ce_2S_3.

Application of the coating is performed according to the technology described in Example 1.

Application of the outer ceramic layer is performed by way of an electron-beam evaporation of a ceramic material, containing zirconia, yttria and cerium sulfide, preliminarily mixed and compacted into discs 68.5 mm in diameter, which are placed in one of the crucibles of the evaporator.

The rate of deposition (condensation) of metallic layers of the coating is 5.9 μm/min, of the outer ceramic layer - 2.1 μm/min. The general porosity of the outer ceramic layer is 16%, and an average diameter of a single grain 2.1 μm.

The tests for thermal cycling have been performed under conditions described in Example 3. The amplitude of thermal stresses is 565-620 MPa.

The thermal cyclic life time of four-layer coatings equals 1,600 cycles, which is by 550 cycles more than the life time of the same coating, but without additions of cerium sulfide into the outer ceramic layer. The thermal cyclic life time of a three-layer coating (without an aluminide layer), containing cerium sulfide in the outer ceramic layer, is 920 thermal cycles, and that of a two-layer coating of the metal/ceramic type (its composition and thickness are given in Example 3, but with the outer ceramic layer composed of ZrO_2 - 8% by mass Y_2O_3) is 740 cycles.

EXAMPLE 10. Applied on the plate-shaped samples measuring 120x10x1.5 mm, made from a superalloy, con-

taining, % by mass: Cr 22.5; W 7.0; Co 6.0; Mo 4.5; Fe 4.5; Al 3.0; Ti 1.3; and Ni - the balance, is a three-layer coating, including an inner plastic layer Ni - 17,2% b by mass Cr - 3.0% by mass Al - 0.1% by mass Y, 40 μm thick, an oxidation-resistant layer Ni - 17.6% by mass Cr - 13.1% by mass Al - 0.1% by mass Y, 50 μm thick, and an outer ceramic layer ZrO_2 - 25% by mass Y_2O_3 - 0.3% by mass TiB_2, 90 μm thick. The outer ceramic layer also contains two interlayers of metallic zirconium, 4.0 μm thick each, arranged parallel to the surface of the sample made from a superalloy. The distance from the surface of the oxidation-resistant layer to the nearest interlayer is 20 μm, and that between the interlayers - 30 μm.

The technological parameters of application of the coating are similar to those described in Example 7. In application interlayers of metallic zirconium, the process of deposition of the outer ceramic layer is interrupted, the rotating fixtures with samples are positioned over the crucible, where a zirconium ingot is placed, and by way of its evaporation obtained is an interlayer of metallic zirconium on the samples, after which the process of evaporation of ceramics is resumed.

The rate of condensation of metallic zirconium is 1.0 μm/min, and that of the outer ceramic layer - - 3.5 μm/min. The general porosity of the outer ceramic layer is 15%.

The conditions of testing for thermal shock resis-

tance are described in Example 2.

In comparison with a coating of the similar thickness and composition, but without interlayers of metallic zirconium, the instant coating has a 1.4-times greater thermal cyclic life time - 584 thermal cycles. A three-layer coating of the same composition, but without titanium diboride in the outer ceramic layer, has failed after 330 thermal cycles. A two-layer coating, containing an oxidation-resistant layer Ni - 17.6% by mass Cr - 13.1% by mass Al - 0.1% by mass Y, 90 μm thick, and an outer ceramic layer ZrO_2 - 25% by mass Y_2O_3, 90 μm, thick , has endured 170 thermal cycles. A coating, containing interlayers of metallic zirconium in the outer ceramic layer had on the metal/ceramic interface, after testing for oxidation-resistance at a temperature of 1,000°C during 500 hours, a layer of alumina Al_2O_3 1.9 μm thick, whereas a traditional two-layer coating - 3.8 μm.

EXAMPLE 11. Applied on the plate-shaped samples made from a superalloy (the form and composition are given in Example 10) is a three-layer coating, whose thickness and composition are given in Example 10. The only difference is the fact that the outer ceramic layer, 110 μm thick, has a composition ZrO_2 - 6% by mass Y_2O_3 - 0.5 by mass Ce_2S_3.

The technology of deposition of the coating is given in Example 9. The rate of condensation of metallic

layers of the coating is 5.6 μm/min, and that of the outer ceramic layer - 1.9 μm/min. The general porosity of the outer ceramic layer is 17% , the average diameter of single grains - 3.3 μm.

The conditions of performing the thermal cyclic tests are given in Example 2.

The thermal shock resistance of the present coating is 390 thermal cycles, whereas that of the same coating, but without sulfide in the outer ceramic layer - 355 thermal cycles. A two-layer coating of the metal/ceramic type, containing an oxidation-resistant layer Ni - 17.6% by mass Cr - 13.1% by mass Al - 0.1% by mass Y, 90 μm thick, and an outer ceramic layer ZrO_2 - 6% by mass Y_2O_3, 110 μm thick, has failed after 250 thermal cycles.

EXAMPLE 12. Applied on the cylindrical samples made from a superalloy (the form of the samples and composition of the superalloy are indicated in Example 2) is a three-layer coating, into an outer ceramic layer of which introduced are four interlayers of metallic zirconium. The coating includes an inner plastic layer Co -24.0% by mass Cr - 4.1% by mass Al - 0.1% by mass Y, 45 μm thick, an oxidation-resistant layer Co - 27.7% by mass Cr - 10.5% by mass Al - 0.1% by mass Y, 50 μm thick, and an outer ceramic layer ZrO_2 - - 8% by mass Y_2O_3, 123 μm thick.

The thickness of an interlayer, nearest to the

surface of the outer ceramic layer, is 3.0 μm, the other interlayers having a thickness of 2.5 μm each. The distance between the surface of the oxidation-resistance layer and the nearest interlayer of metallic zirconium is 23 μm, and between each of the interlayer - 21 μm.

The technological parameters of deposition of the coating are given in Example 1.

The rate of condensation of metallic layers of the coating is 5.1 μm/min, that of the outer ceramic layer - 2.1 μm/min, and that of metallic zirconium - 1.0 μm/min. The general porosity of the outer ceramic layer is 14%.

The tests for thermal shock resistance have been conducted under conditions described in Example 2.

The thermal shock resistance of the three-layer coating, containing interlayers of metallic zirconium in the outer ceramic layer, covers 593 thermal cycles. A similar coating without interlayers in ceramics has failed after 425 thermal cycles. A two-layer coating, containing an oxidation-resistant layer Co - 27.7% by mass Cr - 10.5% by mass Al - 0.1% by mass Y, 95 μm thick, and an outer ceramic layer ZrO_2 - 8% by mass Y_2O_3, 120 μm thick, has withstood 320 thermal cycles.

The metallographic analysis of the samples withdrawn from the tests after 400 thermal cycles has shown that the thickness of a layer of alumina Al_2O_3 in

a three-layer coating, whose outer ceramic layer contains interlayers of metallic zirconium, is 3.0 μm, whereas in a three-layer coating of the same composition and thickness, but without interlayers of metallic zirconium, the thickness of a layer of alumina Al_2O_3 equals 4.5 μm.

EXAMPLE 13. Applied on small-size blades of an aircraft gas turbine (their dimensions and composition of the superalloy are given in Example 4) is a three-layer coating, in whose outer ceramic layer of ZrO_2 - 25% by mass Y_2O_3 - 5.0% by mass Ce_2O_3 50 μm thick, introduced are seven interlayers of metallic zirconium, 0.5 μm thick each.

The distance between the surface of the oxidation-resistant layer and the interlayer of metallic zirconium, nearest to it, as well as the distance between each of the interlayers is 6 μm.

The thickness and composition of metallic layers of the coating are given in Example 4. Special features of the coating deposition technology are given in Example 10.

The rate of condensation of the outer ceramic layer is 2.5 μm/min, and that of metallic zirconium - 0.8 μm/min. The general porosity of the outer ceramic layer is 17%.

The conditions of carrying out thermocyclic tests of blades with coatings are given in Example 4.

Subjected to testing are also a three-layer coating

without interlayers of metallic zirconium and containing no cerium sulfide in the outer ceramic layer, and a two-layer coating described in Example 4, having an outer ceramic layer of ZrO_2 - 25% by mass Y_2O_3.

According to the results of the thermal cyclic tests, they are classified as follows:

(1) a three-layer coating with interlayers of metallic zirconium - 435 thermal cycles;

(2) a three-layer coating without interlayers of metallic zirconium - 375 thermal cycles;

(3) a three-layer coating without interlayers of metallic zirconium and without cerium sulfide - 320 thermal cycles;

(4) a two-layer coating - 264 thermal cycles.

EXAMPLE 14. Applied on cylindrical samples (the size is given in Example 2) made from a superalloy of the following composition, % by mass: Cr 16.0; Mo - 4.1 ; W 9.5; Al 1.4; Ti 1.4; C 0.06 and Ni - the balance, is a three-layer coating of the metal/ceramic type, including an inner plastic layer Co - 22.3% by mass Cr - 2.5% by mass Al - 0.1% by mass Y, 35 μm thick, an oxidation-resistant layer Co - 27.2% by mass Cr - 10.5% by mass Al - 0.1% by mass Y, 45 μm thick, and an outer ceramic layer, 65 μm thick. On the first group of samples applied is an outer ceramic layer ZrO_2 - 8% by mass Y_2O_3, on the second group ZrO_2 - 8% by mass Y_2O_3 - 1.8% by mass TiB_2 , on the third group ZrO_2 -

- 8% by mass Y_2O_3 - 2.5% by mass Ce_2S_3, and on the fourth group ZrO_2 - 8% by mass Y_2O_3 with two interlayers of metallic zirconium, each 2 μm thick (the distance between interlayers and between the surface of the oxidation-resistant layer and an interlayer nearest to it, is 20 μm).

Special features of the technology of application of the coating are given in Example 1. The rate of deposition of metallic layers of the coating is 5.3 μm/min, that of the outer ceramic layer- 2.0 $\pm$ 0.3 μm/min, and that of metallic zirconium 1.0 μm/min.

The corrosion life time of the abovementioned coatings is determined by way of an isothermic oxidation of the samples, on whose surface applied is a mixture of salts, imitating an ash of the gas turbine fuel of the following composition, % by mass: Na_2SO_4 66.2; Fe_2O_3 20.4; NiO 8.3; CaO - 3.3; V_2O_5 - 1.8. The ash in the form of a suspension, prepared on ethanol, is applied on the coatings. The specific concentration of the ash on the surface of the outer ceramic layer is 10-12 mg/cm^2.

Tests are conducted at temperatures of 750 and 850°C during 9-18 thousand hours. A layer of ash is renewed every 250 hours. The corrosion resistance of coatings is evaluated by means of metallographic analyses and by a weighing method by losses of mass of the samples in case of spalling of the outer ceramic layer. The time required till starting a failure of the metallic

oxidation-resistance layer is considered a life time of the coating.

Considered as a base coating is a two-layer condensation system, comprising an oxidation-resistant layer Co - 27.2% by mass Cr - 11.6% by mass Al - 0.1% by mass Y, 80 μm thick, and an outer ceramic layer ZrO_2 - - 8% by mass Y_2O_3, 65 μm thick. The test results are given in the Table below.

Corrosion life time, thousand hours

Coating (outer ceramic layer)	Test temperature 750°C	850°C
Base, two-layer (ZrO_2 - 8% by mass Y_2O_3)	14	6.5
Three-layer (ZrO_2 - 8% by mass Y_2O_3)	18*	10.5
Three-layer (ZrO_2 - 8% by mass Y_2O_3 - 1.8% by mass TiB_2)	18*	12.8
Three-layer (ZrO_2 - 8% by mass Y_2O_3 - 2.5% by mass Ce_2S_3)	18*	11.5
Three-layer (ZrO_2 - 8% by mass Y_2O_3 with two interlayers of Zr)	18*	13.7

* - not failed. Tests are stopped.

The present invention has been described above purely by way of example, and modifications can be made within the scope of the invention.

CLAIMS

1. A metal/ceramic protective coating for superalloy articles, comprising an outer ceramic layer comprising metal oxides; an oxidation-resistant layer comprising an M-Cr-Al-Y alloy, where M comprises Ni, Co, Fe, or a combination thereof, wherein the Al content of the oxidation-resistant layer is 7.5-14.0% by weight; and an inner plastic layer comprising M-Cr-Al-Y alloy, where M comprises Ni, Co, Fe, or a combination thereof, lying between the oxidation-resistant layer and a surface of a superalloy article, the Al content of the inner plastic layer being 2.5-5.5% by weight, and wherein the ratio of the thickness of the oxidation-resistant layer and the inner plastic layer is 4.0-1.0.

2. The protective coating according to Claim 1, wherein the outer ceramic layer comprises yttria-stabilized zirconia.

3. A protective coating according to Claim 2, wherein the outer ceramic layer also comprises a subgroup IVa metal diboride, with the following ratios of components, % by weight:

TiB_2 or ZrB_2 or HfB_2	- 0.3 - 6.0;
Y_2O_3	- 5.0 - 25.0;
ZrO_2	- the balance.

4. A protective coating according to Claim 2, wherein the outer ceramic layer also comprises cerium sulphide, with the following ratio of components, % by weight:

Ce_2S_3	- 0.5 - 5.0;
Y_2O_3	- 6.0 - 25.0;
ZrO_2	- the balance.

5. A protective coating according to Claim 2, 3 or 4, wherein the outer ceramic layer also comprises metallic zirconium in the form of interlayers, 0.5-4.0μm thick, lying in the outer ceramic layer, parallel to a surface of the article, the minimum distance between the surface of the oxidation-resistant layer and an interlayer of metallic zirconium nearest to it being 6.0μm, wherein there is at least one interlayer of metallic zirconium.

6. A protective coating according to Claim 5, wherein the outer ceramic layer comprises at least four interlayers of metallic zirconium, the thickness of each interlayer being 2.5 - 3.0μm, and wherein the distance between each of the interlayers is 20-23μm, and the distance between the surface of the oxidation-resistant layer and an interlayer nearest to it is 20-23μm.

7. A protective coating according to Claims 1 to 6, further comprising an aluminide layer with an aluminium

content of 15 - 35% by weight, and a thickness of 5.0 - 45.0μm, lying between the inner plastic layer and a surface of a superalloy article.

8. A protective coating of the metal/ceramic type for articles from superalloys, comprising an outer ceramic layer on the basis of metal oxides, an oxidation-resistant layer from an alloy M-Cr-Al-Y, where M is Ni, Co, Fe, taken separately or in combination, with a content of Al in the oxidation-resistant layer of 7.5-14.0% by mass, and an inner plastic layer from an alloy M-Cr-Al-Y, where M is Ni, Co, Fe, taken separately or in combination, arranged between the oxidation-resistant layer and a surface of an article from the superalloy, with the content of Al in the inner plastic layer of 2.5-5.5% by mass, the ratio of thicknesses of the oxidation-resistant layer and the inner plastic layer being 4.0-1.0.

9. A protective coating according to Claim 8 wherein the outer ceramic layer on the basis of yttria-stabilized zirconia also comprises one of diborides of metals of subgroup IVa of the Periodic system of elements, with the following ratio of components, % by mass:

TiB_2 or ZrB_2 or HfB_2	- 0.3 - 6.0;
Y_2O_3	- 5.0 - 25.0;
ZrO_2	- the balance.

10. A protective coating according to Claim 8, wherein the outer ceramic layer on the basis of yttria-stabilized zirconia also comprises cerium sulfide, with the following ratio of components, % by mass:

Ce_2S_3	- 0.5 - 5.0;
Y_2O_3	- 6.0 - 25.0;
ZrO_2	- the balance.

11. A protective coating according to Claim 8 or 9 or 10, wherein the outer ceramic layer on the basis of yttria-stabilized zirconia also comprises metallic zirconium in the form of interlayers, 0.5-4.0μm thick, arranged in the outer ceramic layer, parallel to an article surface, the minimum distance between the surface of the oxidation-resistant layer and an interlayer of metallic zirconium, nearest to it, being 6.0μm, and the number of interlayers of metallic zirconia - at least one.

12. A protective coating according to Claim 11, wherein the outer ceramic layer on the basis of yttria-stabilized zirconia, comprises at least four interlayers of metallic zirconium, the thickness of each interlayer being 2.5 - 3.0μm, and the distance between each of the interlayers, as well as the distance between the surface of the oxidation-resistant layer and an interlayer, nearest to it, being 20-23μm.

13. A protective coating according to Claims 8 to 12, wherein it also comprises an aluminide layer with the content of aluminium 15 - 35% by mass, 5.0 - 45.0μm thick, arranged between the inner plastic layer and the surface of an article from a superalloy.

14. A protective coating according to any of the preceding Claims, as identified in the description, examples and accompanying drawings.

15. A protective coating substantially as herein described with reference to the accompanying drawings.

16. A protective coating substantially as herein described with reference to any of the foregoing examples.

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Examiner's report to the Comptroller under Section 17 (The Search Report)

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Relevant Technical fields

(i) UK Cl (Edition K) C7F (FGA, FGZ, FPCX, FPDX, FPEX, FBAX, FBBX, FBXX)

(ii) Int Cl (Edition 5) C23C

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI

Search Examiner

P G BEDDOE

Date of Search

26 MARCH 1991

Documents considered relevant following a search in respect of claims 1-16

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
Y	GB 2,206,358 A (UKAEA) see especially Claim 1; page 4 lines 1-13 and Example 1	1,8
Y	GB 2,226,050 A ~~GB 2,206,050 A~~ (UNITED TECHNOLOGIES) see especially Claim 1	1,2,8
Y	GB 2,159,838 A (UNITED TECHNOLOGIES) see especially Claim 1	1,8
Y	EP 0,266,299 A2 (UNITED TECHNOLOGIES) see especially Claim 1	1,2,8
Y	EP 0,185,603 A1 (UNITED TECHNOLOGIES) see especially pages 11-13	1,2,8
Y	US 4,851,300 A (UNITED TECHNOLOGIES) see especially Claim 1; column 2 line 33 - column 3 line 44	1,8

SF2(p)

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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